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## Layer-by-Layer Growth of 2D Quantum Superlattices (NBIT III)

Jiwoong Park  
CORNELL UNIVERSITY

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Final Report

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**PI and Co-PI information:**

Korean Principal Investigator (KPI)		US Principal Investigator (USPI)	
Full Name (age)	Hee Cheul Choi (44)	Full Name (age)	Jiwoong Park (41)
Nationality	Korea	Nationality	Korea (US Resident)
Affiliation (department)	POSTECH (Chemistry)	Affiliation (department)	Cornell University (Chemistry and Chemical Biology)
Position	Professor	Position	Associate Professor
Telephone	+82-54-279-2130	Telephone	1-773-834-3179
Fax	+82-54-279-3399	Fax	1-607-255-4137
E-mail	choihc@postech.edu	E-mail	jwpark@uchicago.edu
Address	San31, Hyoja-Dong, Namg-Gu, Pohang, Korea	Address	Baker Laboratory Ithaca, NY 14853 USA

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**Summary:**

In this report, we describe our progress in new synthesis, fabrication and characterization techniques for building quantum superlattices using 2D materials as the building blocks. Specifically, we develop methods that allow **i)** large-scale growth of aligned-crystal graphene and high quality TMDs monolayers such as MoS<sub>2</sub> and WS<sub>2</sub>; **ii)** wafer-scale atomic layer assembly method for building atomically-precise superlattice and heterostructures, **iii)** lateral and clean patterning of 2D materials for atomically-thin circuitry and **iv)** novel physical properties in both 2D-only and 2D/organic hybrid systems. The development here realizes a set of powerful tools that would enable novel quantum structures with high precision and flexibility beyond conventional methods. Moreover, it provides the solutions for current major barrier for 2D materials (e.g., limited scalability) while preserving their unique properties, which provide the key foundation for leading these new materials into interdisciplinary and industrial applications. This work is funded by the AFOSR grant (FA2386-13-1-4118) “Layer-by-Layer Growth of 2D Quantum Superlattices”.

**Introduction:**

Semiconductor superlattices are one of the most important elements in science and technology over the past century, with their applications ranging from generating two-dimensional electron gases, light-emitting diodes, to quantum cascade lasers. While these systems are conventionally fabricated using layer-by-layer growth including chemical vapor deposition (CVD), pulsed laser deposition and molecular beam epitaxy, such growth methods require certain substrates and structural and chemical compatibility for interface formation (e.g. lattice match and low solubility), which limits their flexibility in exploring new types of structures. Alternatively, using two-dimensional (2D) materials, such as graphene, hexagonal boron nitride (hBN) and transitional metal dichalcogenides (TMDs), as the building blocks for this can potentially extend

the flexibility without losing structural precision and scalability due to their unique properties. On the one hand, they can be easily generated as monolayer with atomic thickness (only one to three atoms); on the other hand, they only form van der Waals (vdW) interaction between layers or with substrates. When they are grown/assembled layer-by-layer, these properties allow atomic precision in vertical composition design while allowing a variety of material structures and substrates, because no bonding is required for the formation of the interfaces (e.g., no lattice match is required). In addition, these atomically-thin 2D materials can be laterally-patterned into functional atomically-thin circuitry, allowing artificial designs of the materials in all directions. Another exciting prospect of the assembly of 2D materials would be realized when combining them with other material systems such as organic materials, which would allow new hybrid material system to be generated.

In order to fully utilize these advantages of 2D materials in building quantum superlattice, we developed methods that provide solutions to the primary obstacle in this field. Currently, 2D superlattices are mainly generated using either direct sequential growth of TMDs by CVD, or layer-by-layer re-stacking of exfoliated 2D crystals. The former provides large-scale production and pristine interfaces but poor lateral uniformity and structural controllability, which largely limits its applications. In contrast, re-stacking of exfoliated samples has good structural controllability and therefore has led to many great achievements in fundamental physics from Hofstadter butterfly to valley Hall effect. However, it requires delicate techniques and is limited to micron-meter in lateral size, a barrier that impedes further development and integration with other fields. In the lateral direction, on the other hand, there is only few works done on patterning of 2D materials and the integration of graphene, hexagonal boron-nitride (hBN) and TMDs for building atomically-thin circuitry. Methods for contamination-free patterning and forming good contacts between 2D materials are still at the initial stage. In this final report, we describe our progress in addressing the above problems and demonstrate the integration of different 2D materials, both vertically and laterally, as well as hybrid with organic materials, which would provide the essential basis for bringing 2D materials into inter-disciplinary as well as industrial applications. Our work will be discussed in the following parts: Large-scale growth of high quality graphene and TMDs monolayers (**A**, **B**, **C**); assembly of large-scale 2D materials with atomic-scale controllability (**D**, **E**); lateral patterning and designing of atomically-thin circuitry (**F**, **G**); Application and integration of 2D materials with organic materials (**H**).

## Experiment, Results and Discussion:

### A. Polycrystalline graphene with single crystalline electronic structure<sup>1</sup>

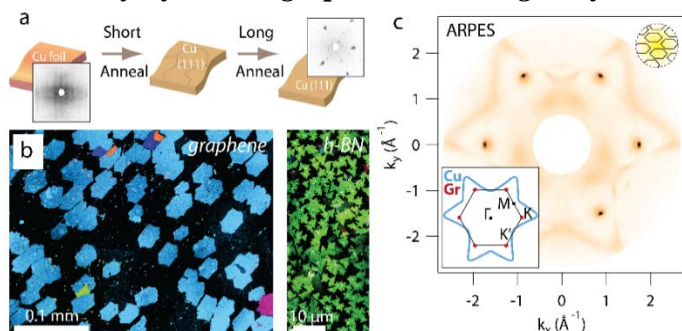


Fig. 1 (a) Process for generating Cu (111) surface as a template for aligned growth. Long time annealing leads to uniform (111) surface. (b) False color DF-TEM images show uniform crystal orientation for graphene and hBN. (c) ARPES Fermi surface map of graphene (beam size 90  $\mu\text{m}$ ).

We developed a method for growing ML films of graphene and h-BN with a uniform lattice orientation up to center-meter scale. These films were grown on Cu (111) surface using CVD method. The crystal structure of Cu (111) serves as a template for the graphene/hBN growth and thus “lock” the crystal orientation for most grains, forming single-crystal like film even when they are grown polycrystalline. In Fig. 1b, we show the dark-field TEM images for both graphene and hBN,

where each false color represents a specific crystallographic orientation. In partial-coverage graphene and hBN, the majority of the islands have similar orientations across the imaged area ( $\sim 300\text{ }\mu\text{m}$ ), which is representative of the entire sample. This is further confirmed by angle-resolved photoemission spectroscopy (ARPES) on continuous samples. In Fig. 1c, the ARPES map shows only one set of six dirac points of graphene, indicating a single crystalline electronic structure in our films. Having a defined in-plane crystal orientation would enable studies of many lattice-related properties. Moreover, we can hence control the out-of-plane crystal structure of the stacked film in a simple way and produce unique properties such as circular dichroism (See part **D**).

### **B. High-quality single-layer graphene grown on amorphous $\text{SiO}_2$ substrates<sup>2</sup>**

CVD growth of graphene in large-scale using copper foils as the substrates and catalysis has led to a tremendous boost in the 2D materials field. However, detaching graphene from the metal substrates and transferring to target substrate often generate defects such as wrinkles, cracks and metal ions that serious degrade the quality. Here we report that Cu catalysis can be supplied in vapor form to help growing graphene on a  $\text{SiO}_2/\text{Si}$  substrate (Fig. 2a), a standard substrate that is heavily used in modern silicon technology. In Fig. 2b, we show that the Raman spectrum of the as-prepared graphene has the G and  $\text{G}'$  peak of monolayer graphene, with only very small defect peak (the D peak). Fig. 2c further shows the flat surface of graphene without the presence of wrinkles and cracks. In Fig. 2d, we fabricate graphene field-effect transistor devices using e-beam lithography. The device shows a sharp Dirac peak of graphene around the origin in resistance as a function of the back-gate voltage after vacuum annealing, which indicates the graphene has good quality and intrinsic properties. Mobility values are extracted to be  $\sim 700\text{ cm}^2/\text{Vs}$ , comparable to the value typically reported when grown on metal substrate. The large improvement from vacuum annealing indicates that, besides wrinkles and metal ions, the polymer that is used to pattern the graphene might be another major contamination. We address this problem in part **G**.

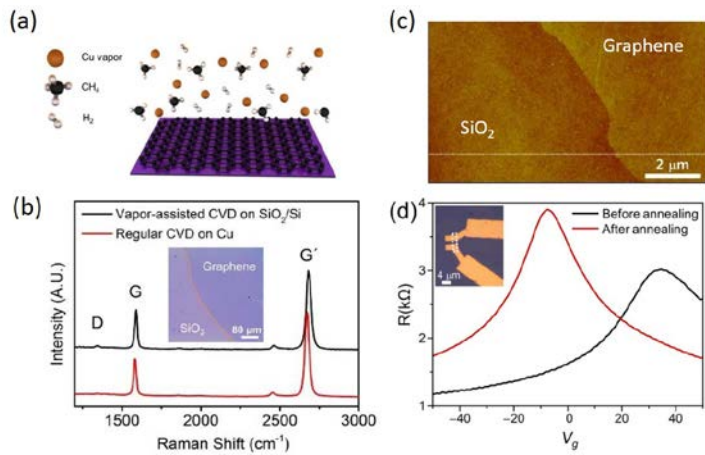


Fig. 2 (a) Schematics of copper vapor assisted growth of graphene on  $\text{SiO}_2/\text{Si}$  substrate. (b) Raman spectra of vapor assisted graphene v.s. standard graphene grown on Cu. Inset: optical image of graphene grown on  $\text{SiO}_2/\text{Si}$ . (c) AFM image of graphene grown on  $\text{SiO}_2$  surface. (d) Resistance v.s. back-gate voltage of our graphene FET. The Dirac peak of graphene is sharp and close to zero back-gate voltage after annealing to remove residues of the polymer used for e-beam lithography.

### **C. High-mobility monolayer TMD films with wafer-scale homogeneity<sup>3</sup>**

Transition metal dichalcogenides are a large family of the form  $\text{MX}_2$  (M=transition metal, X=chalcogenides), which can be generated as atomically-thin layers having diverse properties from metallic, semiconducting to superconducting. Having a method to grow them in monolayer on a large scale would allow fully-integrated atomically-thin circuitry with metal, semiconductors, insulators, a difficult limit for traditional semiconductors. Unlike graphene, however, growth of TMDs using existing CVD method has limited spatial uniformity and electrical performance. We

Fig.3 (a) Schematics of the MOCVD growth. (b) Photos of MoS<sub>2</sub> (left) and WS<sub>2</sub> (right) grown on 4" fused silica. Bare fused silica is shown on the left half of the wafer in each photo. (c) Conductance v.s. top gate. Inset: device geometry (top-left) and photo of the entire array of ~8,000 devices on 4" SiO<sub>2</sub>/Si wafer. (bottom-right) (d) Histogram of the on- and off- state conductance of 99 randomly-chosen devices both show sharp distribution and a good on/off ratio of 10<sup>6</sup>.

reported the growth of semiconducting monolayer films of MoS<sub>2</sub> and WS<sub>2</sub> using metal-organic chemical vapor deposition (MOCVD) on silicon oxide on a 4-inch wafer scale, with both excellent electrical performance and structural continuity maintained uniformly over the entire films. Fig. 3a schematically describes the MOCVD process. We use metal organic precursor as the source of transitional metal atoms, and hydro-carbonyl chalcogenides for the chalcogenides atoms. All the precursors are introduced to the chamber in gas phase, which allows precise concentration control using mass flow controller (MFC) and provides an uniform environment in the

furnace during the growth. Fig. 3b shows photos of MoS<sub>2</sub> and WS<sub>2</sub> grown on 4" inch wafers, where uniform color is observed (bare fused silica is shown at the left half of each wafer for comparison). In Fig. 3c, we further fabricate MoS<sub>2</sub> transistors using as-grown MoS<sub>2</sub> on SiO<sub>2</sub>/Si. We fabricad more than 8,000 devices on a 4" inch wafer (see bottom-right inset), and the representative conductance-gate voltage curve of our devices shows n-type semiconductor behavior. The device yield is >99%, and the medium value of mobility is measured as ~29 cm<sup>2</sup>/Vs at room temperature, an order of magnitude better than those of other CVD methods (typically few cm<sup>2</sup>/Vs) and comparable to exfoliated samples. Fig. 3d plots the histogram of the on- and off- state conductance of 99 devices distributed over the wafer. Both states show sharp distribution with a medium on- and off- ratio of 10<sup>6</sup>. This result is a direct indication of the high quality and uniformity in our TMD films.

#### D. Chiral atomically thin films<sup>4</sup>

The non-covalent bonding nature between 2D material layers provides a new degree of freedom to create interlayer translations or rotations in 2D stacked films, unlike in conventional epitaxy-grown materials. This interlayer degree of freedoms, especially the rotation, can greatly modify the band structure. We reported a new method to produce twisted bi-layer graphene (tBLG) with controlled interlayer angle ( $\theta$ ) in large scale and found strong circular dichroism (CD) in these tBLG, depending on how the layers are rotated relative to each other. Fig. 4(a) shows our process. We start with the aligned graphene grown on Cu (111) (See section A. **Polycrystalline graphene with single crystalline electronic structure**) and cut the graphene/copper foil in half. Since the two pieces have same crystal orientation, we can rotate one of the pieces with  $\theta$ , right- or left- handed, and then stack them together. Fig. 4 presents the ellipticity ( $\Psi$ ) spectra (or CD spectra), measured from the left-handed (red) and right-handed (blue) twisted bilayer graphene samples with  $\theta = 16.5^\circ$ . Here,  $\Psi$  is proportional to the absorption



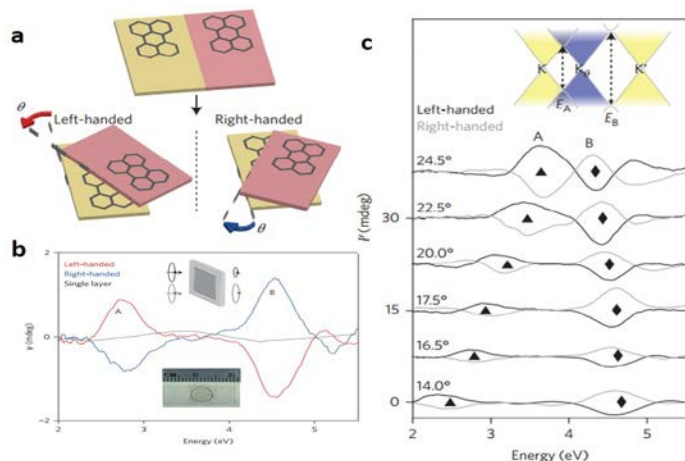


Fig.4 (a) Schematics of the process for making angle- and handedness- controlled twisted bi-layer graphene (tBLG). (b) Representative circular dichroism (CD) absorption spectra of tBLG with same angle ( $\theta$ ) but opposite handedness. The absorbed light shows different handedness at the A and B absorption peaks of tBLG. (c) CD spectra of tBLG with different angles and handedness. All angles show CD on the A and B peak, but the ellipticity ( $\Psi$ ) varies with angle. Inset: band structure of tBLG. Arrows indicates the optical transitions for the A and B absorption peaks with transition energy  $E_A$  and  $E_B$ , respectively.

difference between the left and right circularly polarized light, and is vanishing if there is no CD dependence (such as single layer graphene in Fig. 4b). As shown, while both tBLG show two absorption peaks, A and B, with the sign of  $\Psi$  being opposite, the overall spectra are flipped between left- and right-handed graphene, indicating there is CD dependence on the structural handedness. Fig. 4c further shows that CD is universal in tBLG, while the amplitude of  $\Psi$  and the peak energy can be tuned according to  $\theta$ . The technique developed here is an important step toward the ultimate “materials by design”, which would allow one to control the film’s properties by structural design as demonstrated here.

### E. Building wafer-scale films layer-by-layer by stacking three-atom-thick semiconductor<sup>7</sup>

Stacking atomically-thin layered materials into van der Waals heterostructures is one of the most exciting approaches for realizing atomically-designed thin films, and many works have proved it to be a viable route for realizing previously inaccessible heterostructures with novel physical properties. However, there has been no large-scale stacking method that maintained the intrinsic properties of the building blocks while producing pristine interlayer interfaces, which limits the use of this approach to small-size proof-of-concept demonstrations. We reported a newly-developed method of programmed vacuum stacking, where a series of wafer-scale, three-atom-thick semiconductor layers with different chemical compositions ( $\text{MoS}_2$ ,  $\text{MoSe}_2$ , and  $\text{WS}_2$ ) are mechanically peeled from the growth substrate and then stacked to the next layer under vacuum. This peel-and-stack process can be repeated until the desired number of layers is achieved, as shown in the simplified schematics of the process in Fig. 5a. Fig. 5b shows a

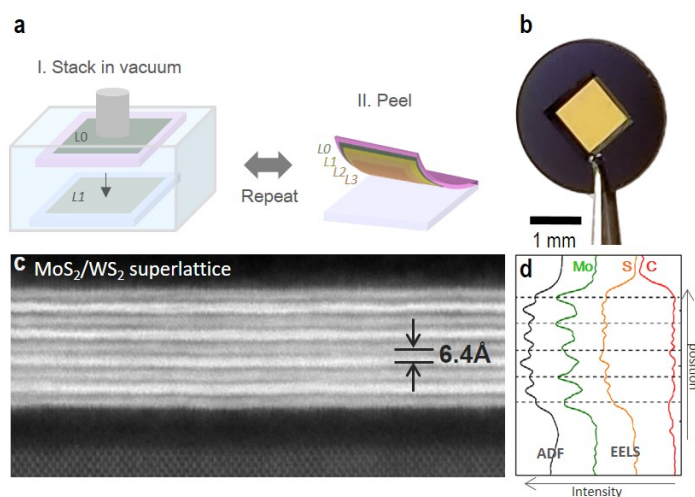


Fig. 5 (a) Simplified schematics of the programmed vacuum stacking process. We mechanically peeled the monolayer TMDs grown on  $\text{SiO}_2$  by MOCVD and stacked atop of another layer under vacuum. The peel-and-stack steps can be repeated until the targeted layer number is reached. (b) A freestanding 7L- $\text{MoS}_2$  suspended over a  $1 \times 1 \text{ mm}^2$  hole. (c) A cross-sectional ADF-STEM image of a 9-layer  $\text{MoS}_2/\text{WS}_2$  superlattice film stacked by our method. Dark:  $\text{MoS}_2$  monolayers; bright:  $\text{WS}_2$  monolayers; intensity profile in (d). (d) EELS spectrum for Mo (green), S (orange) and C (red). There is no detectable carbon signal within our film under the resolution of our instrument.

stacked 7L-MoS<sub>2</sub> that is suspended over a 1×1 mm<sup>2</sup> square hole in the middle of a TEM chip. The freestanding film is thinner than 5 nm, with one of the highest aspect ratio (length/thickness ~ 0.2 million) ever reported for freestanding semiconductor films, which also indicates that our film has excellent structural quality and mechanical strength. In Fig. 5c, we further show a cross-sectional STEM image of a representative superlattice film assembled by vertically stacking nine layers of wafer-scale TMDs alternating between MoS<sub>2</sub> (5 layers, dark) and WS<sub>2</sub> (4 layers, bright). The image shows that the interfaces between adjacent layers remain clean and free of bubbles or wrinkles, having a constant interlayer distance of 0.64 nm (measured center to center), which is consistent with the value expected for MoS<sub>2</sub>/WS<sub>2</sub> with a non-zero interlayer rotation angle. The EELS data in Fig. 5d further confirms the composition, and shows a very low signal for carbon (red curve) within the film near the detection limit of our instrument. Altogether, the data demonstrate that we have successfully produced high-quality semiconductor films with atomic-scale programmability and pristine interfaces, and that such films can be separated from the substrate as ultra-thin freestanding films. The process developed here provides a general approach to stack atomically-thin materials, and could potentially be used for vertical assembly of hybrid materials and devices, where non-layered materials, such as organic films and self-assembled nanostructures, are stacked vertically, layer by layer, along with 2DBBs and atomically-thin circuits. These exciting potentials will accelerate the discovery of novel materials, as well as the large-scale development of ultrathin multifunctional integrated circuitry.

#### F. Atomically-thin Ohmic edge contacts between two-dimensional materials<sup>5</sup>

With the decrease of the dimensions of electronic devices, the role played by electrical contacts is ever increasing, which eventually become dominating in the overall device volume and total resistance. This is especially problematic for monolayers of atomically-thin layered materials. Therefore, we developed a scalable method to fabricate graphene 1D contacts to TMDs, where the junctions are laterally

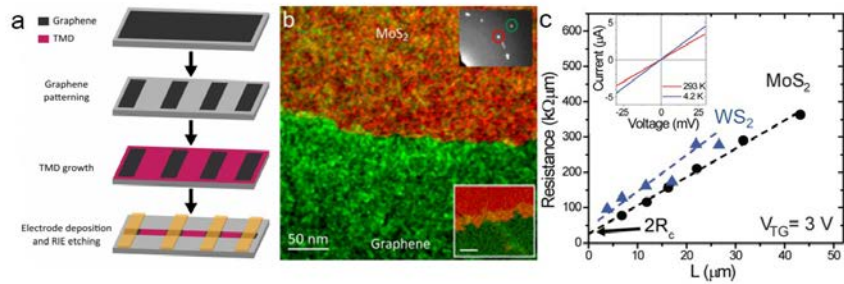


Fig. 6 (a) Schematics for fabricated lateral contact between graphene and MoS<sub>2</sub>. (b) EELS mapping of the graphene/MoS<sub>2</sub> lateral contact. Inset: (top) diffraction pattern for MoS<sub>2</sub> (red) and graphene (green); (bottom) overlap contact when growth condition is not optimized. (c) Transfer length measurement for graphene/WS<sub>2</sub> contact and graphene/MoS<sub>2</sub> contact. Inset: source-drain current versus bias voltage at room temperature (293K, red) and helium temperature (4.2K, blue).

connected and show an ohmic contact resistance as low as ~30 kΩμm. Fig. 6a shows the process schematics for this: we first grew monolayer graphene on copper foil using CVD method, then transferred to SiO<sub>2</sub>, followed by growing the monolayer TMDs using MOCVD method. Under the optimal growth condition, the TMDs only grows on top of SiO<sub>2</sub> but barely on graphene, forming a nicely-stitched lateral junction. The patterned graphene/MoS<sub>2</sub> film is then fabricated into electrical devices for further characterizations. Fig. 6b shows the EELS mapping of our lateral junction (main panel), while the inset shows an overlapping junction (colored orange) that forms when the growth is not optimized. To confirm the contact resistance R<sub>c</sub>, we performed a transfer length measurement (TLM) to extract the value as shown in Fig. 6c. It is observed that the contact resistance is ~30 kΩμm regardless whether it is WS<sub>2</sub> or MoS<sub>2</sub>, showing that our method here could be general for these semiconducting TMDs. Fig. 6c inset further shows the source-drain current *versus* voltage curve of the devices at room temperature and at 4.2 K. In



both cases, we observe linear J-V relation, which indicates the contacts between graphene and MoS<sub>2</sub> are ohmic down to helium temperature. The technique demonstrated here for making edge contacts to semiconducting TMDs provides a versatile, stable, and scalable method for forming low-volume, low-resistance contacts for atomically thin electronics, which could be attractive for flexible and optically transparent electronics.

### G. Patternable large-scale molybdenum disulfide atomic layers grown by gold-assisted chemical vapor deposition<sup>6</sup>

While atomically-thin layered materials exhibit extraordinary physical properties that are promising for novel future electronics, the use of conventional process such as photolithography largely degrades their performance as mentioned in section B. Therefore, it is critical to develop a set of new fabrication procedures that is specially designed for atomically-thin layered materials so as to preserve these good properties. In this work, we grew few-layer MoS<sub>2</sub> films on top of gold substrate using two-step CVD method, which allows us to obtain patterned MoS<sub>2</sub> by patterning the gold substrate ahead of the growth. Fig. 7a schematically describes the proposed growth mechanism: first, when we flow molybdenum hexacarbonyl vapor into the furnace, the Mo atom diffuse into gold substrate and form a thin layer of Mo-Au on the surface. In the second step, H<sub>2</sub>S is introduced to sulfurize the Mo-Au alloy layers into few-layer MoS<sub>2</sub> films, which is typically 2-3 layers as shown in the cross-sectional TEM image in Fig. 7b as well as supported by additional AFM measurements. The Raman spectrum shown in Fig. 7b inset confirms the film is MoS<sub>2</sub>, with two prominent peaks that corresponds to the E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> peak of MoS<sub>2</sub>. The as-grown patterned MoS<sub>2</sub> can then be transferred by etching the gold substrate. To show this capability, in Fig. 7c we grew a few-layer MoS<sub>2</sub> film on a gold substrate that is pre-patterned into the shape “MoS<sub>2</sub>” (see top). In the bottom optical microscope image of Fig. 7c, we show the same few-layer MoS<sub>2</sub> film after transferred to SiO<sub>2</sub>/Si substrate, which preserve the pattern we designed for it. Our work here offers a simple yet relatively clean process for patterning MoS<sub>2</sub>, which would be an important step toward atomically-thin electronics and circuitry that retains the intrinsic properties of the materials.

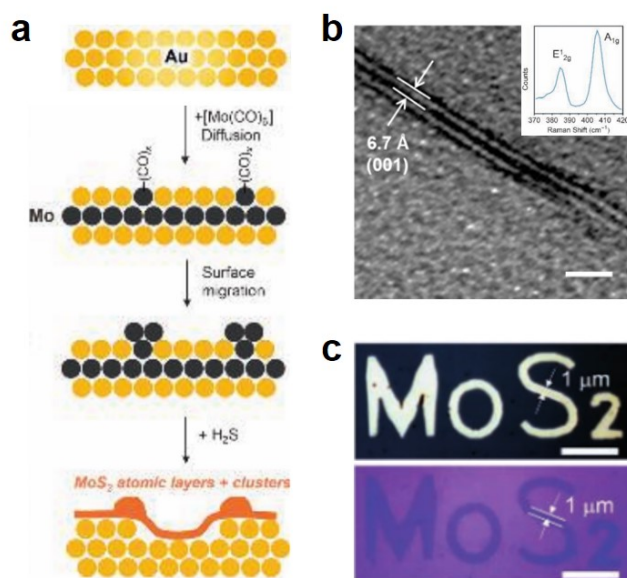


Fig. 7 (a) Schematics of the growth mechanism for the two-step gold-assisted CVD method. (b) Cross-sectional TEM image of the as-grown MoS<sub>2</sub>, typically 2 to 3 layers. Scale bar: 2 nm. Inset: Raman spectrum of the few-layer MoS<sub>2</sub>, showing clear E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> peak. (c) Patterned growth of MoS<sub>2</sub> on gold (top) and after transferred to SiO<sub>2</sub>/Si substrate. Scale bar: 10 μm.

### H. Soft epitaxy of organic crystals on graphene template substrate (on-going project)

Change of molecular packing and crystal growth direction is important to modulate properties of organic crystal. However, specific directional growth of organic crystal remains as a big challenge. Here we report a directional growth of conjugated organic crystal, where graphene is used as a template to control its growth direction through  $\pi$ - $\pi$  interaction. Selected molecule is p-terphenyl, which has three aromatic ring linked by a single bonding at para- position. Physical

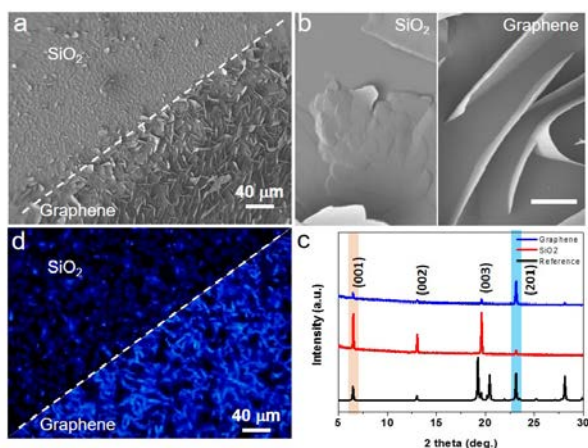


Fig. 8 (a) SEM image of p-terphenyl grown on SiO<sub>2</sub> (top-left) and graphene (bottom-right). (b) Zoom-in SEM image of (a). Scale bar: 4 μm. (c) XRD data for p-terphenyl grown on SiO<sub>2</sub> (red), graphene (blue) and a reference p-terphenyl crystal (black). (d) Photoluminescent image on p-terphenyl on SiO<sub>2</sub> and graphene. This is a different sample from (a).

vapor transport (PVT) method was used to crystallize p-terphenyl on different substrates. Fig. 8a shows the SEM image of p-terphenyl crystal grown on SiO<sub>2</sub> (left) and graphene (right), where very different morphology on each substrate is clearly observed. In the zoom-in image in Fig. 8b, it is shown that, on graphene, p-terphenyl is mostly grown in the vertical direction, forming a sharp disk morphology. In contrast, on SiO<sub>2</sub> substrate it tends to form crystal parallel to the substrate without a specific morphology. This difference in crystal structure is further supported by the XRD data in Fig. 8c: XRD pattern of p-terphenyl crystal grown on SiO<sub>2</sub> exhibit three main peaks for the (001), (002), and (003) planes, which indicates the packing of p-terphenyl molecule is perpendicular to SiO<sub>2</sub>. On the contrary, the strong peak corresponding to the (201) plane

(at 23.12°) for the p-terphenyl crystal on graphene strongly suggests the packing of p-terphenyl molecule is lateral on graphene. The different crystal direction would allow us to control the physical properties of the materials. For example, Fig. 8d shows strong photoluminescence (PL) enhancement of p-terphenyl crystal grown on graphene, which comes from the correlation between incoming light and the dipole moment of the molecule (*i.e.*, crystal plane). While here we only demonstrate the template growth of p-terphenyl, similar behavior is expected for other organic molecules or even nano-crystals. The ultimate goal would be growing these materials with controlled structures on 2D materials and stack these 2D/molecules hybrid composites layer-by-layer into novel hybrid material systems, which has the exciting potentials for discovery of novel materials, as well as development of multifunctional electronics.

## I. Conclusion

This project was devoted to develop new synthesis, fabrication and characterization techniques for building novel material system using 2D materials as the building blocks. We successfully developed new growth process that allows the synthesis of a variety of 2D monolayers with large-scale uniformity and high material quality. Based on these techniques, we further developed new stacking methods to assemble these atomically-thin papers into artificial thin films. This allows us to generate novel physical properties with these 2D materials, such as the giant chiral response in twisted bi-layer graphene, or construct innovative structures that are inaccessible before. In addition, we utilize the lateral-patterning technique on 2D materials to generate 1D edge contact between graphene and TMDs, which shows promising performance for future atomically-thin circuitry. We also show preliminary results of soft epitaxy of conjugated organic crystals on 2D materials, which is a step toward the exciting prospect of building 2D/organic hybrid systems. Our work here would offer a set of important tools for 2D materials to take the current proof-of-concept only demonstrations into practical technological and interdisciplinary applications.

## List of Publications and Significant Collaborations

a) papers published in peer-reviewed journals,

1. L. Brown, E. B. Lochocki, J. Avila, C.-J. Kim, Y. Ogawa, R. W. Havener, D. K. Kim, E. J. Monkman, D. E. Shai, H. I. Wei, M. P. Levendorf, M. Asensio, K. M. Shen, J. Park, "Polycrystalline graphene with single crystalline electronic structure", *Nano Lett.* **14**, 5706 (2014).
2. H. Kim\*, I. Song\*, C. Park, M. Son, M. Hong, Y. Kim, J. S. Kim, H. Shin, J. Baik, H. C. Choi, "Copper vapor-assisted direct growth of high quality and metal-free single layer graphene on amorphous SiO<sub>2</sub> substrate.", *ACS Nano* **7**, 6575 (2013).
3. K. Kang\*, S. Xie\*, L. Huang, Y. Han, P. Y. Huang, K. F. Mak, C.-J. Kim, D. A. Muller, J. Park. "High-mobility three-atom-thick semiconducting films with wafer scale homogeneity", *Nature* **520**, 656 (2015)
4. C.J. Kim, A. Sanchez-Castillo, Z. Ziegler, Y. Ogawa, C. Noguez, J. Park, "Chiral atomically thin films", *Nat. Nanotech* **11**, 520 (2016).
5. M. H. D. Guimaraes\*, H. Gao\*, Y. Han, K. Kang, S. Xie, C.-J. Kim, D. A. Muller, D. C. Ralph, J. Park, "Atomically-thin ohmic edge contacts between two-dimensional materials", *ACS Nano* **10**, 6392 (2016)
6. I. Song, C. Park, M. Hong, J. Baik, H. Shin, H. C. Choi, "Patternable large-scale molybdenum disulfide atomic layers", *Angew. Chem. Int. Ed.* **53**, 1266 (2014).

b) manuscripts submitted but not yet published

7. K. Kang\*, K.H. Lee\*, Y. Han, H. Gao, S. Xie, D. A. Muller, J. Park, "Building wafer-scale films layer-by-layer by stacking three-atom-thick semiconductors", under external review, *Nature* (2016).

c) provide a list of any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.

1. 8 patents applied (U.S.: 4, Korea: 3, Japan: 1)
2. MOCVD growth of wafer-scale transitional metal dichalcogenides monolayers transferred to an international company.